Emissions Related to Munitions Firing: A Case Study of Nitrogen Oxides, Volatile Organic Compounds, and Energetic Residue from Detonable Munitions

R. Szostak and K. Cleare

Overall, the detonation of munitions represents an environmentally clean reaction. Six kilotons of energetic materials were expended in this case study during training in 1996. These included nitrocellulose (55 percent), trinitrotoluene (TNT) (30 percent), nitroglycerine (5 percent), nitroguanidine (4 percent), dinitrotoluene (DNT) (3 percent), and Royal Dutch Explosive (RDX) (3 percent). Based on previously reported test data (BangBox), energetic detonation emissions of environmental concern were calculated to be less than 1 percent. This residue contains nitrogen oxides (88 percent), a mix of volatile organic compounds (11 percent), and possibly undetonated RDX (<1 percent). Preliminary assessment of emissions produced by munitions in this study indicates that both nitrogen oxide (NOX) and volatile organic compound (VOC) emissions are low relative to other NOX and VOC producing activities including emissions from biogenic (natural) sources. Though the amount of undetonated RDX is low, further work is needed to validate this number and determine whether this source represents any significant health or environmental impact. © 2000 John Wiley & Sons, Inc.

***R. Szostak** works with the Army Environmental Policy Institute on Active Range environmental issues. Dr. Szostak is also a professor of chemistry at Clark Atlanta University in Atlanta, Georgia. **K. Cleare** also works with the Army Environmental Policy Institute on Active Range environmental issues.* *The views expressed in this article are those of the authors and do not necessarily reflect the official policy or position of the Department of the Army, Department of Defense, or the U.S. Government.*

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INTRODUCTION

Energetic material constitutes a primary chemical component of training munitions. They include explosives and propellants. When initiated properly, energetic material evolves large volumes of hot gas in a short time. The difference between explosives and propellants is the rate of the reaction. For explosives, reaction rates are fast and produce a very high shock pressure in the surrounding medium. In propellants, the rate is slower, producing lower pressure, which is sustained over a longer period of time. Nitroglycerin, nitrocellulose, nitroguanidine, trinitrotoluene (TNT), and Royal Dutch Explosive (RDX) are common explosives. The U.S. Army uses substantial amounts of these chemicals in training to maintain readiness of its forces.

Other components found in training munitions, but not covered in this article, include the pyrotechnics. Compounds in this class may contain halogens (fluorine, chlorine), chalcogens (sulfur), and metals (aluminum, magnesium, barium, lead, zinc).

Major products from detonation of energetics are considered to be limited to environmentally benign species; carbon dioxide, nitrogen, and water. Varying amounts of carbon monoxide, mixed nitrogen oxides (NOX), volatile organic compounds (VOCs), and residual energetic material may also be released. The amounts are dependent on the efficiency of the detonation and elemental makeup of the round. There have been recent concerns expressed by regulators and the public over emissions generation through training activities. These concerns center on whether emission may represent a human health hazard to communities surrounding training ranges as well as represent a threat to drinking water sources. To identify the validity of these concerns, a more detailed analysis of the nature and amount of emissions from energetics is warranted.

Methodologies have not been developed to assess the emissions from training activities. However, emissions factors for open detonation of energetic materials from demilitarized weapons have been developed using closed-chamber (BangBox) test data. These factors have been applied in this study to energetics used in training munitions to provide an approximation of air emissions from these activities, which may be of environmental concern. Though this study represents an approximation of the types and amounts of emissions that might occur from training related activities, the results can be used to begin assessing the direction that needs to be taken in managing training ranges to encourage more environmentally sustainable practices.

Methodologies have not been developed to assess the emissions from training activities.

TRAINING RANGE CASE STUDY

The data used for this case study reflects information obtained at one installation for munitions training occurring in fiscal year (FY) 1996 as reported in the Training Ammunition Management Information System (TAMIS). The data used in this study does not constitute an average of Army training activities nor should it be used to represent munitions use for any of the active training ranges. This data also does not represent

unusually excessive amount of activity but only activities that have occurred on one installation during peacetime.

ENERGETIC CHEMICAL USE

In 1996, the installation under study expended approximately 30 million munitions rounds during that year of training. Within these rounds was contained 6 kilotons of chemicals consisting mostly of energetic materials including nitroglycerine, nitrocellulose, nitroguanidine, TNT, DNT, and RDX. A breakdown of these amounts of these energetic chemicals used in the primary training activities is shown in **Exhibit 1.**

EMISSIONS FROM DETONATION

Energetic materials are not directly released into the environment during munitions training activities because the very efficient detonation process which defines explosive materials. Though energetics considered as propellant material undergoes deflagration as opposed to detonation, both processes were considered comparable for this study. Major products formed through detonation of energetic materials are carbon dioxide, nitrogen, and water.

Virtually no chemical reaction is 100 percent efficient, including detonation-type reactions. Minor products could consist of VOCs (defined as saturated hydrocarbons, ethylene, propylene, acetylene, and other unsaturated hydrocarbons, benzene, toluene, other aromatics), NOX, carbon monoxide, and certain unconsumed explosives.

Exhibit 1. Energetic Chemical Components of Munitions Fired in 1996 (Calculated Using Data Taken from the Munitions Items Disposition Action System [MIDAS] Database)

	# rounds (from TAMIS)	Tons RDX	Tons TNT	Tons DNT	Tons nitrocellulose	Tons nitroglycerin	Tons nitro guanidine
Small arms ammo	*28,464,956*	0	0	14	1,430	151	97
Propellant munitions	*821,996*	0	0	16	770	127	54
Propellant charges and increments	*141,221*	0	0	103	824	0	46
HE cartridges	*558,363*	127	69	20	198	4	12
HE projectiles and warheads	*221,839*	4	1,713	0	1	1	0
HE rockets	*28,423*	20	13	0	47	34	0
White phosphorous rounds	*18,817*	1	0.5	0.5	6	2	1
TOTAL	***30,255,615***	**152**	**1,795**	**153**	**3,276**	**319**	**210**

Complex compounds produced (those larger than the energetic material) were not observed in the BangBox studies, which is consistent with detonation theory. Thus, complex compounds would not be expected as typical range contaminants from active training activity. This information is important as it can minimize the number of analytes needed to be considered when range air/soil/water sampling or monitoring is required.[1] Acceptance of this premise could result in substantial cost savings when surveying potential chemical contaminants in range soil and water samples.

Assembled munitions contain other fill in addition to energetic materials to improve specific characteristics.

Assembled munitions contain other fill in addition to energetic materials to improve specific characteristics. They consist of hydrocarbon-containing compounds (phthalates), halides (chloride/chlorate or fluoride salts), chalcogens (sulfur in black powder and sulfates) and various metals (potassium in black powder, oxidizers including aluminum and zinc, and projectiles composed of lead [Pb]). At the present time, emission products from detonations containing these chemicals remain to be investigated with the rigor used for determining the emissions produced from the energetic materials. This study does not attempt to provide any analysis of emissions for these munitions components. Fundamental chemistry would suggest that those emissions products would include simple compounds such as HCl, SO_2, and the various metal oxides and other particulate matter. The BangBox study summarized in the following section has confirmed the formation of HCl and SO_2 from the detonation of assembled munitions containing those elements. Quantification of those amounts remains unknown.

PRIOR FIELD TESTS

In 1996, a field test at Camp Grant, Illinois was performed in which 140 rounds of 3-inch Stokes trench mortars were individually detonated.[2] Background samples, soil and water samples were collected, and the amount of residue released from those detonations was determined. Detonation was found to be very efficient as no residue was detected. Negative evidence does not constitute sufficient proof and therefore a better experimental design was needed.

INFORMATION AND METHOD USED FOR THE QUANTITATION

Emissions Factors

An emission factor is defined as the amount of that individual chemical produced by a detonation divided by the total mass of the energetic material before detonation. Emissions factors for detonation of energetic materials and waste munitions have been previously determined using the BangBox located at Dugway Proving Grounds in Utah.[3] The BangBox consists of two sections: an inflatable, 930 m3, 16.5-m-diameter hemispherical test chamber made from a flexible polyvinyl-coated polyester fabric and a 5.5 x 2.1 x 2.5 m building (airlock). The chamber is inflated by two high-capacity blowers; six fans spaced 60∞ apart that circulate the air in the test chamber to produce a homoge-

neous pollutant mix that is sampled with instruments in the chamber and attached to the air lock. The Environmental Protection Agency (EPA) has accepted these BangBox derived emission factors as representative of those which could be determined from open-air detonations. Emissions factors for unconfined, encapsulated, and water suppressed detonations have been calculated in that report, as have the emissions factors for open burns.[4]

The encapsulated detonations were identified as lower in efficiency relative to the other types of detonations studied in the BangBox and would represent a more conservative (possibly worst-case) value. The encapsulated detonation emissions factors were used in this study. Though emissions factors derived from each individual type of training round should produce a more precise number, these were not available at the time of this study. Studies under the direction of the Army Environmental Center examine actual training rounds and will ultimately provide validation of the work presented here.

The significant figures used generally provide an indication as to the level of certainty in the final numbers reported in this work. Overall, confidence is limited to order of magnitude for the results reported here.

A list of the VOC analytes formed from detonation and their emission factors used in this study are shown in **Exhibit 2.**

Using the Emissions Factors

The total quantity of individual chemical emissions produced at an installation from munitions usage can be estimated by using experimentally determined (BangBox) emission factors, the number of rounds fired, and the amount of chemical components in each round:

Chemical emissions produced = (emission factor) $\times$ Σ {(organic chemical component in round) $\times$ (# rounds)}

NOX Emissions Factor

The NOX emission factor was calculated from the BangBox data. The percentage N occurring as NOX (1.78 percent), and the percentage NO in NOX (71.0 percent) were experimentally determined. The NOX emission factor is calculated to be 0.04. The methodology used to arrive at this number is shown below.

In order to convert the BangBox information into a usable emission factor for NOX for this study required the following set of calculations:

From the equation:

N in the energetic material => N_2 + NOX

100 pounds of N in the energetic material will convert to 1.78 pounds of N as NOX (the rest being converted to N_2). The molecular weight of NOX (average of NO+NO_2, containing 71 percent NO, 29 percent NO_2)= 34.6. Therefore the number of pounds of N in one pound of NOX is 14/34.6= 0.405. The emission factor calculated for use in this study for NOX: 0.0178/0.405 = 0.04 pounds NOX formed per pound of N in the energetic material detonated.

Exhibit 2. VOC Analytes and Their Emissions Factors* for Encapsulated Detonations; also Provided Are the Emissions Factors for NOX and the Energetic Residues

	Emissions Factors
VOCs	
Sat. HC	0.000055
Ethylene	0.000256
Propylene	0.00005
Acetylene	0.0003
Other unsat. HC	0.000061
Benzene	0.000069
Toluene	0.000026
Other aromatics	0.000042
NOX	0.04
Energetic Residues	
RDX	0.00161
TNT	0.00000029 [1]
DNT	0.00000029 [1]

* From Mitchell, W.J., &.Suggs, J.C. Emission factors for the disposal of energetic materials by open burning and open detonation (OB/OD) (EPA/600/R-98/103).USEPA.

1. Neither TNT nor DNT were observed in the BangBox studies. In order to provide an estimate it was assumed that the levels were at the detection limit for general energetic materials. Thus the MQL emissions factors provided in Table 3-1 of Mitchell and Suggs for RDX, PETN, HMX were used for TNT/DNT at the advice of the BangBox report authors.

Number of Rounds Used

Training ranges track type and amount of munition rounds expended. The Training Ammunition Management Info System (TAMIS) can provide these data. Chemical constituents and amounts for each muntion type can be retrieved from the Munitions Items Disposition Action System (MIDAS) database. An abbreviated example of the type of information gathered from TAMIS is shown in **Exhibit 3.** The rounds expended were grouped by Department of Defense Identification Code (DODIC) and the number of rounds in that group summed. This sum was defined as the total number of rounds expended for this system and used for the subsequent calculations.

Examples of the chemical information found in the MIDAS database and how they were used in this study are shown in **Exhibit 4.** From MIDAS, the chemical grouping (PEP, supplemental charge, etc.), the

Exhibit 3. Example of Information Obtained from the Training Ammunition Management Info System (TAMIS), at One Installation in 1996 and the Information (Total Rounds) Obtained

System	DODIC	Nomenclature	Rounds expended	Total rounds
M2a2m3a2	A111	CTG 7.62mm blank	1,152,983	
M577a3	A111	CTG 7.62mm blank	644,559	
M1a1	A111	CTG 7.62mm blank	617,549	
M1	A111	CTG 7.62mm blank	262,572	**2,677,663**
M2a2m3a2	A131	CTG 7.62mm ball	2,994,539	
Hmmwv	A131	CTG 7.62mm ball	2,937,331	
M1a1	A131	CTG 7.62mm ball	2,934,030	**8,865,900**
M577a3	A143	CTG 7.62mm ball	866,859	
M901a1	A143	CTG 7.62mm ball	208,066	**1,074,925**

weight, the type of chemical, and percentage of each of the individual chemical components were entered into the spreadsheet. From this information the number of pounds per round could be calculated for

Exhibit 4. Information Extracted from the MIDAS Database, as well as the Calculations Used to Determine the Total Number of Pounds of Each Chemical Component of a Weapon System Used at One Installation in 1996

	High energy cartridges		**Total number of rounds** 558,363		
B542	CTG 44mm HEDP M430		**Number of rounds** 337		
				Grams/round*	Total pounds**
	Propellant	*4.6 grams*	%		
		NC	77.21	3.6	3
		Nitroglycerin	19.44	0.9	1
		Ethyl centralite	0.6	0.0	0
		Ba(NO3)2	1.4	0.1	0
		KNO3	0.75	0.0	0
		graphite	0.6	0.0	0
	PEP	*37.5 grams*	%		
		RDX	98.5	36.9	27
		Stearic acid	1.5	0.56	0

* (% 3 # grams/100); **(grams/round 3 # rounds/454)

each chemical. This number was multiplied by the number of rounds expended at the site in FY 1996 for that DODIC number to obtain the total number of pounds of each energetic chemical.

Using the TAMIS FY 1996 data for one installation and emissions factors for encapsulated detonation (a conservative approach as discussed in a previous section) reported by Mitchell and Suggs, the cumulative amount of VOC, NOX, and unconsumed explosive can be estimated for each type of munition training activity. A sample calculation is shown in **Exhibit 5** for VOC and RDX and **Exhibit 6** for NOX.

Exhibit 5. Sample Calculation to Determine the Amount of VOCs and Residual RDX Emitted from Use of High Energy Cartridges

	High Energy Cartridges		
Organic/energetic components	*Σ pounds*		
Nitrocellulose (NC)	395,842		
Nitroglycerin (NG)	8,678		
Nitroguanine (Ngu)	109		
Dibutyl-phthalate	23,184		
Diphenylamine	4,564		
DNT	40,985		
RDX	253,499		
TNT	137,993		
Tetryl	4		
ethylcentralite	302		
PETN	0		
Misc. organics	4,566		
Total pounds organic components	869,726		
		Emissions factors	Total pounds*
Sat.hydrocarbons (HC)		0.000055	48
Ethylene		0.000256	223
Propylene		0.00005	43
Acetylene		0.0003	261
Other unsat. HC		0.000061	53
Benzene		0.000069	60
Toluene		0.000026	23
Other aromatics		0.000042	37
Total VOCs produced			**747**
RDX residue		0.00161	**408****

*(emissions factor × total pounds of organic components); **(RDX emission factor × total pounds RDX)

Exhibit 6. NOX Emissions Calculated for fhe Components of the Munitions Containing Nitrogen

High energy cartridges		Total rounds expended 558,363	
N-containing Compounds	**% N**	**Total lbs N Compounds**	**Total lbs N***
NC*	13.3	395,842	52,647
Nitroglycerin	18.4	8,678	1,579
Nigroguanidine	53.84	109	59
Phthalates	0	—	—
Diphenylamine	8.3	4,564	479
DNT	16.7	40,985	6,845
KNO3	13.86	6,761	937
Sr(NO3)2	13.2	2	0
Ba(NO3)2	10.7	56	6
RDX	37.84	253,499	95,924
TNT	18.5	137,993	25,529
tetryl	24.4	4	1
Ethylcentralite	3	302	9
PETN	17.5	0	0
tetracene	74.4	0	0
* % N assumes gun cotton			
Σ Total lbs N			183,932
Lbs of NOX produced			*7,357*

*Because the emissions factor for NOX has been calculated for the weight amount of NOX produced per weight of nitrogen (not total weight of nitrogen containing energetic), the total weight of nitrogen in each of the energetic materials must be calculated first before applying the emission factor.

Dioxins, Furans, and Other Analytes

BangBox studies indicated that neither dioxins nor furans were identified as emissions from detonating rounds. Sensitivity levels were 10^{-10} for furans and 10^{-11} for dioxins. Dioxins were concluded to be a potential emissions product only in cases where chloride containing compounds were found in combination with organic material. Few munitions contain chlorine as a chemical component. For those contain-

ing chlorine, the primary product identified in the BangBox study was shown to be HCl and not dioxins. Further study is needed to determine whether dioxins are emitted from training munitions containing chloride compound.

Phthalates are also components of training munitions. Since they are not energetic materials they were treated as "misc. organics" in all calculations used to determine the VOC emissions. The potential for phthalate residue was not addressed in this report (phthalates are common contaminants in analytical laboratories as well as in the environment and therefore it was not possible to quantify any unreacted phthalate as emissions at this time).

RESULTS OF DATA ANALYSIS AND COMPARISON OF EMISSIONS WITH OTHER ACTIVITIES

Six kilotons of energetic materials were expended at the installation during training in 1996. These included nitrocellulose (55 percent), TNT (30 percent), nitroglycerine (5 percent), nitroguanidine (4 percent), DNT (3 percent), and RDX (3 percent). This breakdown is graphically depicted in **Exhibit 7**.

Total emissions consist mainly of CO_x, H_2O, and N_2 along with less than 1 percent of chemicals with environmental concern. This breakdown is shown in **Exhibit 8** (left side). Air emissions of environmental concern resulting from the detonation were calculated to be very low (45 tons). The small amount of residue calculated from detonation of the energetic

Exhibit 7. Chart Indicating the Relative Amounts of Individual Energetic Materials Used in Training Activities at One Installation in 1996

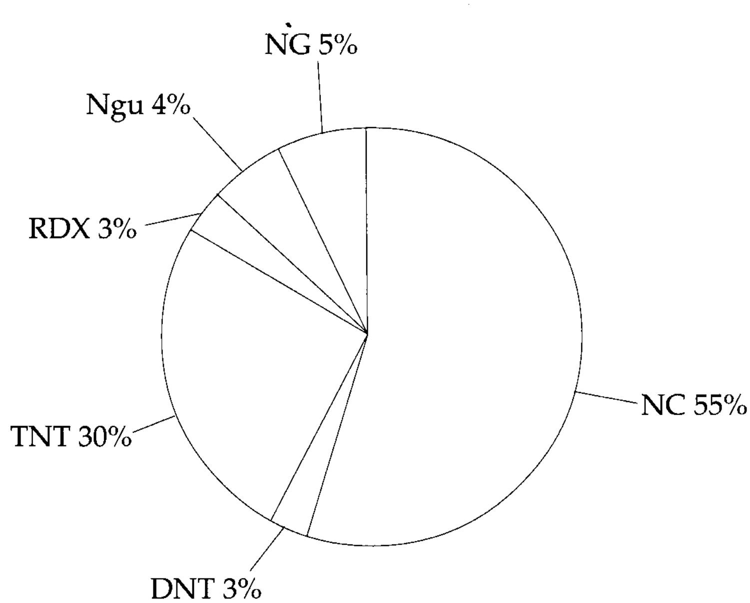
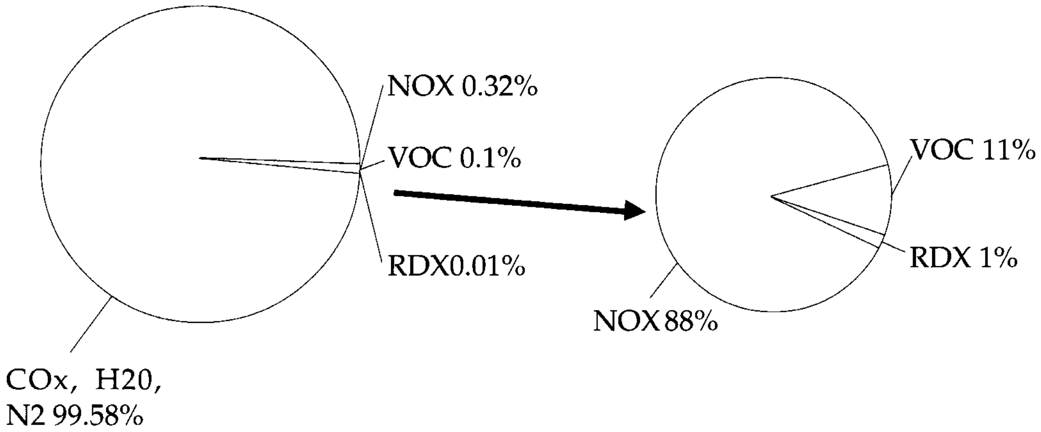


Exhibit 8. Relative Amounts of the Emissions after Detonation (Left) Compared to all Emissions, (Right) Those of Environmental Concern



component contained only nitrogen oxides (88 percent), a mix of volatile organic compounds (11 percent), and RDX (>1 percent) and is shown in Exhibit 8 (right). Since no other energetic material was observed as an emission product in the BangBox studies, the potential cause for concern for their presence at levels below the detection limit was addressed in this study by considering the detection limit for energetics in calculating the potential for emission to be observed. The results obtained using such a conservative approach further confirm that these chemicals do not represent any substantive environmental concern.

The individual residue components are discussed in this section in descending order of mass calculated (i.e., NOX>VOC>RDX>TNT,DNT) and the results are compared to emissions from other relevant sources.

Leading Contender: NOX

The greatest quantity of emissions generated as a by-product of detonation is NOX. In this test case approximately 80,000 pounds (40 tons) of NOX are released to the atmosphere from munitions over one year of training (FY 1996). **Exhibit 9** provides a breakdown based on munition family for the amounts of NOX expelled. Use of high energy projectiles and warheads constitute the largest portion of NOX emissions at this site. Small arms use follows second on the list.

Comparison with Other NOX Sources

NOX emissions are monitored for both stationary and nonstationary sources by EPA and the individual state environmental agencies. Major

sources of NOX emissions include power plants (stationary) and vehicle exhaust (nonstationary). **Exhibit 10** provides a list of NOX emissions for both sources in the greater Atlanta Metropolitan area, the most densely populated area of the state of Georgia. Data from the 1990 survey are presented and represent the latest validated numbers provided by Georgia Department of Natural Resources.[5]

Information from monitoring sites in other less populated parts of the state generally more typical of areas surrounding major training ranges has also been collected for stationary sources. **Exhibit 11** summarizes the information on stationary NOX emissions in other Georgia counties. These data can be used to compare with the average daily emissions from munitions training. To provide a bracket around the level of NOX emissions, the counties with the highest NOX emissions and the least are also listed in the table.

To normalize the data for comparison purposes, the emission densities are used. Emissions density is defined as the number of tons of a compound emitted per day per 1,000 sq. miles. To calculate emissions density, the daily emissions for a location is divided by surface area over which that emission is occurring. The use of emission densities has the advantage of making the numbers more meaningful for direct comparison. For example, the District of Columbia ranks the lowest in emissions relative to the states. However, if area is considered (i.e., emissions density is calculated), it qualifies as the highest concentration in NOX emissions.

The emissions density of NOX for the state of Georgia is 29.49 tons/day/1,000 square miles.[6] The District of Columbia has an emissions density of 772 tons/day/1,000 sq. miles. The emissions density for the munitions training activities is calculated to be 0.25 tons/day/1,000 square miles based on the size of the installation in which training is occurring.

Exhibit 9. NOX Emissions Based on Individual Munition Types

	# of rounds	Nitrogen containing component total (lbs)	Annual NOX emissions (lbs)
Small arms ammunition	28,464,956	449,660	19,148
Propellant munitions	821,996	294,289	12,532
Propellant charges and increments	141,221	257,945	10,984
HE cartridges	558,363	183,932	7,357
HE projectiles and warheads	221,839	637,177	27,133
HE rockets	28,423	45,331	1,930
Rocket practice, smoke	40,449	40,708	1,733
Simulator flash artillery	386,854	2,407	102
WP/PWP	18,817	3,405	145
Total rounds	**30,000,000**		**80,000 lbs/yr** (= 40 tons)

Exhibit 10. Emissions Data Comparison, Atlanta Metro Area 1990 Base Year Nitrogen Oxides Summary in Tons/Day Compared with the Training Range NOX Emissions (Averaged to Tons/Day) (see State of Georgia Department of Resources 1990 Validated Emissions Data)

Point sources	121.34 (tons per day)
Area sources	25.74
Highway mobile sources	304.04
EPA off road mobile	65.35
Aircraft and Railroad	22.26
Total	538.73
munitions training activities	0.11 (tons per day average)

NOX emission from active training appears to be less than the emission produced naturally from the environment. Not all pollution comes from human-centered activities. A portion of NOX emissions is generated from the vegetation and trees. Biogenic (natural) sources of NOX constitute 0.95 tons/day/1,000sq. miles in the state of Georgia.[7]

NOX may be emitted at the firing points and the impact area during the course of training. Its movement in the environment is dependent on dissipation in the air which may dilute the concentrations to well below environmental limits. The rate at which NOX would be dissipated during a training event is dependent on the meteorological conditions of the day and was not considered in this article.

Exhibit 11. Assessment of NOX Emissions Broken Down by County for Point Sources Only

County	**Daily average NOX emissions (tons)**
Other Georgia Counties	
Bryan	1.78
Evans	0.43
Liberty	1.62
munitions training activities	0.11
GA counties with the greatest and least point-source emissions	
Bartow	224 (greatest)
Clayton	< one ton (least)

Ways to lessen these emissions would be limited since the presence of nitrogen in the energetic material is key to its energy release. Many of the projectiles are inert rounds, thus NOX emissions are already being minimized at the point of impact.

VOC: Secondary Emission Product

Volatile organics (VOCs), which include hydrocarbons and aromatics formed from detonation of energetic materials, represent another emission from munitions training activities. **Exhibit 12** provides a breakdown based on munitions family for the total amounts of VOCs formed. Both small arms munitions use and high energy projectile are the major contributors to VOC release on a training range.

Relative to other activities the amount of VOCs emitted from munitions training calculated in this study is low at approximately 5.5 tons per year. In the greater Atlanta Metro area, the annual auto exhaust emissions for VOC is 49,000 tons per year. [8]

Like NOX discussed previously, emission densities provide a better source for comparison of pollution data. The emissions density for VOCs from munitions training activities is calculated to be 0.035 tons/day/1,000 sq. miles. The emissions density for biogenic (natural) VOC for the state of Georgia is 77 tons/day/1,000 sq. miles.

Residual Energetic Materials

Unlike NOX and VOC, which dissipate in the atmosphere, residual energetic materials represent solid materials which, when introduced into the environment, can potentially contaminate soil and water systems. **Exhibit 13** provides a listing of the common energetic materials and key physical properties that are relevant to

Exhibit 12. VOC Emissions Based on Individual Munitions Types

	# of rounds	Organic component total (lbs)	Annual VOC emissions (lbs)
Small arms ammunition	28,464,956	3,424,421	2,942
Propellant munitions	821,996	2,040,768	1,753
Propellant charges and increments	141,221	1,965,473	1,688
HE cartridges	558,363	869,726	747
HE projectiles and warheads	221,839	3,437,657	2,953
HE rockets	28,423	252,211	217
Rocket practice, smoke	40,449	289,210	248
WP/PWP	18,817	22,289	19
Total rounds	**30,000,000**		**11,000 lbs /yr** (5.5 tons)

environmental contamination.

Exhibit 14 shows munitions types, number of rounds fired annually, and RDX used and calculated to be unconsumed after firing. **Exhibit 15** shows munition types, number of rounds fired annually, and TNT used and calculated to be unconsumed after firing. This estimate is based on using emissions threshold values as TNT emissions were either not present at all or at some finite amount less than the detection limit. These numbers may be significantly larger than reality as the amount of undetonated TNT may actually be zero. **Exhibit 16** shows munition types, rounds fired annually, and DNT used and calculated to be unconsumed. Like TNT, the emissions factor used is that based on the detection limit (MQL) for energetic materials (represented in the work of Mitchell and Suggs, table of MQLs as RDX, PETN, HMX) since no residual DNT could be detected in the BangBox studies.

RDX Residue

Of the common energetic materials, RDX represents the energetic with potential for the largest amount of residue released into the environment in this test case as it was one of only two energetics detected in the BangBox. The other, PETN, was not a common energetic found in the munitions used for this study. Whether its presence represents an experimental artifact or a potential environmental residue has not been determined. Less than 500 pounds of RDX residue was calculated in this study.

This potential deposition of any RDX residue would be expected to be concentrated in the impact area in the proximity of the target, as this high-energy material is a component of the projectile fill and not of the primer or the propellant. These later munitions components would more likely leave residue near the firing points. Whether these amounts of residual RDX will ever reach the levels calculated here has not been validated nor has it been determined to represent enough quantity to cause environmental concern. Further work in this area is needed.

TNT AND DNT

TNT, DNT, and other energetic material residues could not be detected in the BangBox emissions. Whether TNT, DNT, and other ener-

Exhibit 13. Environmental Properties of Key Energetic Materials

Energetic	Melting Point	Volatility (mmHg@20°C)	Water Solubility*	Environmental half life*	Environmental mobility*
RDX	205°C+	10^{-9}	60 mg/l	Very high	High
TNT	80.1°C+	$2x10^{-4}$	100 mg/l	700 hours- years	Moderate
DNT	66°C++	$5.7x10^{4}$	270 mg/l	48 hours-12 months	Moderate

* See note 9; + See note 10; ++ See note 11.

Exhibit 14. RDX Potentially Unconsumed after Detonation of Rounds Based on Individual Munition Types

	# of rounds	RDX total (lbs)	Annual RDX unconsumed (lbs)
Small arms ammunition	28,464,956	0	0
Propellant munitions	821,996	0	0
Propellant charges and increments	141,221	0	0
HE cartridges	558,363	253,499	408
HE projectiles and warheads	221,839	7,584	12
HE rockets	28,423	39,580	64
White phosphorous rounds	18,817	1681	3
Total rounds	**30,000,000**	302,846 pounds 151 tons	**500 lbs /yr**

getic material residue is actually present or will ever add up to detectable amounts, is at present, academic. However, as an exercise in this study, a worse-case scenario for TNT and DNT was utilized to provide an indication as to how much the amounts below-detection-limit quantities could potentially amount to (if present at all). As shown in Exhibits 15 and 16, both TNT and DNT produced negligible residues even for this worse-case scenario.

IMPACT FOR SUSTAINABLE RANGE MANAGEMENT

The types of emissions products found for energetic materials are limited to CO_2, N_2, H_2O, CO, NOX, VOC, and possible residual RDX. Air

Exhibit 15. TNT Unconsumed after Detonation of Rounds Based on Individual Munition Types (MQL Factors Used; See Text)

	# of rounds	TNT total (lbs)	Annual TNT unconsumed (lbs)
Small arms ammunition	28,464,956	0	0
Propellant munitions	821,996	0	0
Propellant charges and increments	141,221	0	0
HE cartridges	558,363	137,993	.04
HE projectiles and warheads	221,839	3,425,008	1
HE rockets	28,423	25,986	.01
White phosphorous rounds	18,817	892	0
Total rounds	**30,000,000**		**1.0 lb/yr**

Exhibit 16. DNT Unconsumed after Detonation of Rounds Based on Individual Munition Types (MQL Emissions Factors Used; See Text)

	# of rounds	DNT total (lbs)	Annual DNT unconsumed (lbs)
Small arms ammunition	28,464,956	28,809	0.01
Propellant munitions	821,996	32,293	0.01
Propellant charges and increments	141,221	206,551	0.06
HE cartridges	558,363	40,985	0.01
HE projectiles and warheads	221,839	0	0
HE rockets	28,423	0	0
Total rounds	**30,000,000**		**0.1 lb/yr**

emissions of environmental concern calculated in this study for munitions training activities are low even relative to natural NOX and VOC emissions. The need for continual air monitoring of these activities may not be necessary as quantities of these emissions could prove to be undetectable above background.

Further work that is needed includes a better understanding of the source of residual RDX in the BangBox experiments. Though these calculations suggest some RDX may remain after detonation, whether the amount remaining from a detonated source will ever be detectable is unclear and requires further investigation.

The data presented represents a first order approximation of munitions emissions and should provide a beginning to the understanding of the environmental impact of energetic materials. Comparisons should be made with data collected from air, soil and water sampling at individual ranges to confirm the validity of the results found in this study. ❖

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NOTES

1. Examples of a requirement for extensive testing for analytes can be found in the Massachusetts Military Reservation Report—"Draft Completion of Work Report for the Camp Edwards Impact Area Groundwater Quality Study" MMR, Cape Cod, Massachusetts, prepared for National Guard Bureau Arlington, VA, by Ogden Environmental and Energy Services, 239 Littleton Road, Suite 1B, Westford, Mass 01886

2. "Open Burning/Open Detonation UXO Baseline" TRCA at Camp Grant, Illinois, 31 January 1996, Contract: DACA-87-93-C-0048, by Nichols Research Corporation, for US Army Engineer Division, Huntsville.

3. Mitchell, W.J., &.Suggs, J.C. Emission factors for the disposal of energetic materials by open burning and open detonation (OB/OD) (EPA/600/R-98/103). USEPA.

4. Id.

5. State of Georgia Department of Natural Resources 1990 validated emissions data.

6. http://www.epa.gov:80/ttncaaa1/otagii2.pdf.

7. http://www.epa.gov:80/airprogm/oar/emtrnd95/biogenem.pdf

8. See note 5.

9. a) Howard, et al. (1991). 1991 Handbook of Environmental Degradation Rates. Chelsea, MI: Lewis Publishers.

   b) McGrath, C.J. (1995). Review of formulations for processes affecting the subsurface transport of explosives (Technical Report IRRP-95-2). Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station.

   c) Montgomery, J.H. (1996). Groundwater chemicals desk reference. Boca Raton, FL:

   d) CRC Press.

   e) Myers, T.E., & Townsend, D. M. (1997). Recent developments in formulating model descriptors for subsurface transformation and sorption of trinitrotoluene. Annals of the New York Academy of Sciences, 829, 219–229.

   f) Ro, K.S., et al., (1996). Solubility of TNT in water. Journal of Chemical Engineering Data.

10. From Toxicological Profile (ATSDR).

11. 2,6-dinitrotoluene (2,4-DNT) Hazardous Substances Data Bank (ATSDR).